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FORMATION OF POROUS FILMS ON TITANIUM ALLOYS BY ANODIZATION

MECHANICS AND SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION
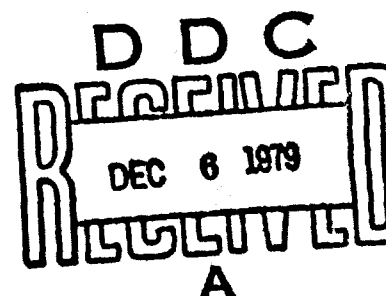
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Surface Treatments	Auger Electron Spectroscopy
Surface Chemistry	Secondary Ion Mass Spectroscopy

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This investigation is part of a program which looks at the effects of surface treatments on surface chemistry and morphology of titanium and titanium alloys. This part considers the effect of surface treatments on the alloy titanium-6 aluminum-4 vanadium which use anodization to produce a porous oxide film.

Porous anodized films on titanium alloys have shown to be advantageous for adhesive bonding and other purposes. Porosity

may be achieved by increasing current density in the anodization bath by increasing the voltage, increasing the concentration of the electrolyte, increasing the temperature, or adding current carrying ions to the electrolyte. In this work, experiments are described in which each of the methods for increasing current density are accomplished. Characterization results on the surfaces of these anodized oxides are shown using scanning electron microscopy, ion scattering spectrometry, secondary ion mass spectrometry, and Auger electron spectrometry. Addition of lithium nitrate to phthalic acid electrolytes causes porosity in anodized films, but the lithium ions do not enter the oxide film.

FOREWORD

This technical report was prepared by W. L. Baun, Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (AFML/MBM), Wright-Patterson Air Force Base, Ohio. This work was initiated under Project 2419, "Nonmetallic and Composite Materials" and was administered by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The Work Unit Monitor is Dr. T. W. Haas.

This report covers work conducted inhouse during the period July 1977 to July 1979.

The author is grateful to James S. Solomon for the Auger electron spectra. Donald Thomas is thanked for his careful experimental work on some of the anodizations.

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INTRODUCTION

With the ever-increasing stringent requirements of operation
at high temperatures and high loading, titanium and its alloys
have been and will be used more and more in the aerospace industry.
The properties of titanium and its alloys can be improved markedly
by the use of a proper surface treatment. Chemical treatments
have been devised which clean the surface, etch the surface, and
create a new bondable oxide surface. Such chemical surface
treatments as PasaJell,[1] VAST,[1] phosphate fluoride,[2] and labora-
tory etches[3] have been described. Such chemical and anodically
formed films have been used to reduce fretting and galling, serve
as a base for dry film lubricants, reduce galvanic corrosion of
other material in contact with titanium, such as aluminum, and
serve as a stable base for adhesive bonding.[4] Work by Moji and
Marceau[5] has shown that porous films formed by anodization methods
provide better bonding surfaces than those prepared by chemical
methods. These authors utilize an anodization technique combin-
ing an oxidizing electrolyte with the addition of fluoride ions
at a pH less than 6 to obtain porous film. The fluoride ion
raises the current density and allows lower voltages to be used
for anodization.

Work in this laboratory, however, shows that the addition of
fluorine to the anodizing electrolyte causes the formation of a
weak boundary layer and subsequent debonding at the oxide/metal
interface.[6] Other workers have also noted the deleterious effects
on aluminum alloys of fluoride ions at the adhesive bonding sur-
face.[7] It appears fluorine can exist in two different states on
the surface. One combined state may be very stable and serve as
a base for adhesive bonding. The other, such as is present upon
anodization in the solution containing fluoride ion, apparently

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does not combine and causes a weak boundary layer. Fluoride ion
is not necessary in the bath to achieve porous films. Porous
films may be achieved by other methods. Methods of preparing
such films on titanium and its alloys will be shown in this report.
Characterization of the surfaces of these films was carried out
using ion scattering spectrometry (ISS), secondary ion mass
spectrometry (SIMS), Auger electron spectrometry (AES), and secon-
dary electron microscopy (SEM).

SECTION II
EXPERIMENTAL

Anodization was carried out on reagent grade materials as noted. A filtered dc power supply was used. ISS and SIMS were performed on a commercial model 520 ion scattering spectrometer (3M Co., St. Paul, MN) to which UTI model 100C quadrupole mass analyzer had been added (Uthe Technology Inc., Sunnyvale, CA). A simple energy filter was added to allow secondary ion mass detection. Auger electron spectrometry was performed using a model 540 thin film analyzer. (Physical Electronics Inc., Eden Prairie, MN).

SECTION III
RESULTS AND DISCUSSION

Porosity of anodized films on titanium may be achieved by
increasing the current density by several methods. These are
to increase the voltage, to increase the concentration of the
electrolyte, or by the addition of current carrying ions to the
electrolyte. Still another possibility is to choose an electro-
lyte to permit simultaneous dissolution and formation analogous to
the aluminum anodization in phosphoric acid where a porous columnar
oxide is created. The easiest method of preparing porous films in
a given electrolyte is to increase the voltage. In most oxide
forming electrolytes when the voltage is increased in steps, a
series of spikes which decay rapidly are observed. When the volt-
age reaches a certain limiting voltage, somewhat lower than the
sparking voltage, an increase in voltage is no longer accompanied
by a decaying spike, but rather shows a constant or undulating
current during which presumably oxide growth is balanced by oxide
dissolution. An example of such an anodization curve is shown in
Figure 1. At each of these voltage steps titanium and its alloys
change colors. These colors are extremely vivid, ranging from
deep blues to brilliant golds. Colored films become visible at
only a few volts, and are very intense in the region of 10 to
100 volts. Assuming approximately 15-20 angstroms per volt in
most electrolytes, this range of thicknesses would be then 150
to 2000 angstroms. Titanium and the other valve metals, when
they form anodic oxide exhibit interference colors which result
in colored oxide films. Light incident on the air/oxide inter-
face is partially reflected and partially transmitted. A portion
of the light that is transmitted through the oxide strikes the
oxide/metal interface, is partially reflected and partially
absorbed. The total light reflected from the oxide/metal combi-
nation may be considered as the sum of two contributions.

The first of these is the light which is reflected at the oxide/
air interface and never passes through the oxide, and the second
contribution consists of light which has passed through the oxide
two or more times before being emitted at the air/oxide interface.
These two portions of light are in phase only in specific wave-
lengths because of path length differences and phase changes
occurring on reflection. The intensity of light reflected is then
a function of the wavelength of the incident light, the thickness
of the oxide film, and the optical properties of both the oxide
and the metal. If this intensity is plotted as a function of
thickness, maxima and minima occur in the oxide color. Thus,
over the range, for instance, from 0 to 100 volts the same colors
may be repeated during this maxima/minima phenomenon. The inten-
sity of the interference colors is a function of the reflectivi-
ties of the air/oxide interface and that of the oxide/metal inter-
face. When strippable anodic oxides on both titanium and tantalum
were removed from the substrates, the colors were different from
the vivid colors on the substrate and much less intense. For
instance, anodized films exhibiting bright blue reflections actu-
ally were pale yellow in transmission.

The rise and decay, as shown in A of Figure 1, is followed at
a certain point by several phenomena illustrated in B. The current
can level off over a range of voltage and be virtually constant or
slowly undulating. It can rise immediately as shown by the dashed
curve and sparking will begin or it can rise slowly as shown by
the dotted curve at which point sparking will also start. Regard-
less of the exact behavior, the titanium oxide appears to become
porous in the region characterized by B. Numerous scanning elec-
tron micrographs were obtained on anodized films showing this
increase in porosity with increase in applied voltage. An example
for two electrolytes is shown in Figure 2. Here examples of
titanium 6 aluminum 4 vanadium were anodized in phosphoric acid

as shown in 1, and in phthalic acid, as shown in 2. The anodized
surfaces shown in A, the surfaces seem to be relatively smooth
with the surface scratches very distinct. When the photographs
shown in A are compared with the photographs of the original
material or of photographs with thinner oxides present on the
surface, it is obvious that an oxide is covering the surface, but
no evidence of porosity is seen. Porosity may exist on such a
fine scale that this magnification is not capable of seeing it.
However, when the anodization voltage is increased to 300 volts,
as in B, the porosity is quite clearly seen. These two electro-
lytes, as well as each electrolyte that was investigated in this
work, produce surfaces having slightly different morphology.

In addition to changing the morphology, increasing the anodi-
zing voltage also chan s the surface chemistry. In Figure 3, the
ion scattering and secondary ion mass spectrometry data are shown
for titanium 6 aluminum 4 vanadium alloy (Ti 6Al 4V) anodized at
50 volts in a mixture of sodium phosphate and phosphoric acid
to form a neutral solution at pH 7. The data are very much like
those obtained earlier from titanium dioxide surfaces. Figure 4
shows the ion scattering and secondary ion mass spectrometry data
for a similar alloy anodized at 100 volts in the same mixture.
The ion scattering spectrum no longer shows the characteristic
titanium/oxygen ratio and the secondary ion mass spectrometry data
shows a marked increase in impurities. ISS spectrum, shown as 1,
is taken immediately upon exposure to the ion beam. The spectrum
shown as 2 is taken 10 minutes after this initial spectrum and
shows that the changes in the oxide film are probably bulk changes
rather than just surface differences. A striking effect on the
positive SIMS data is that the secondary ion yield drops two
orders of magnitude in the porous film as compared to the film
formed at 50 volts. Also, there appears to be some carbonaceous
material in the porous film. This was confirmed by Auger electron

spectrometry, as shown in Figure 5. The surface film was eroded away with an argon beam and spectra taken repeatedly throughout the film. This data showed that the carbon was distributed throughout the porous film. The origin of this carbon is not known but must diffuse out from the bulk during the anodization.

There is a large change in the wetting and spreading characteristics of anodized films with voltage. Figure 6 shows a plot of the water contact angle for two samples exposed to the same anodization conditions in a neutral solution of Na_2HPO_4 plus H_3PO_4. In one sample, the surface was cleaned with a detergent only. The other was cleaned with an abrasive pad plus the same detergent. Although the water contact angle is considerably different in the surfaces cleaned by two different methods, it becomes virtually the same for the anodized surfaces. The spreading of the water is shown here as a function of time for the porous film. Other contact angle measurements show the same behavior of an abrupt drop in contact angle with an increase in anodizing voltage. Similar results are seen when using other electrolytes as shown in Table I. The results shown here are for dilute solutions of the acid and base. Larger concentrations of 1 molar or more show much greater effect on porosity and contact angle. Contact potential measurements, on the other hand, showed no correlation with thickness or porosity whatsoever. In fact, the more porous films caused a great deal of instability in the instrument making measurements very difficult and probably unreliable.

Porosity of the film may also be increased by increasing the concentration of the electrolyte, especially in electrolytes in which the titanium oxide film is somewhat soluble. This increase in concentration increases the current density and decreases the point at which breakdown or sparking is observed. Table I shows

TABLE I

EFFECTS OF INCREASING OXIDE POROSITY
ON H_2O CONTACT ANGLE ON TITANIUM 6 ALUMINUM 4 VANADIUM

Sample	Electrolyte	Voltage	H_2O Contact Angle
197-1	Na_2HPO_4 + H_3PO_4 0.5M pH = 7	20V 50V 100V S*	$74°$ $57°$ $14°$
197-3	NaOH 0.1M pH = 12.4	20V 50V 200V S*	$72°$ $58°$ $53°$
197-4	H_3PO_4 0.1M pH = 1.80	20V 50V 250V S*	$60°$ $54°$ $36°$

*Sparking or hissing

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the breakdown voltage for titanium 6 aluminum 4 vanadium and com-
pares it with values obtained for aluminum, 6061 aluminum alloy
and tantalum anodized in phosphoric acid of four different con-
centrations. The voltage which is noted here, is that voltage
which is recorded when region B is reached in Figure 1. As can
be seen by this Table, an increase in the concentration of the
phosphoric acid leads to a decrease in the breakdown or sparking
voltage. Also, each material exhibits its own particular behavior
pattern with a change in concentration.

Increasing temperature also causes an increase of porosity.
Figure 7 shows the effect of an increase in temperature on the
time versus current curve for the anodization of titanium 6 alumi-
num 4 vanadium in 0.5 molar H_3PO_4. For the temperature range here,
the reaction maintains the characteristic rapid initial increase
and subsequent rapid decay with time. However, as the temperature
increases, the amount of current drawn following this rapid decay
increases. At even higher temperatures the tail is even higher
and during this period there is considerable dissolution and pore
formation in the film.

Still another method of increasing current density and creating
porosity in the oxide film is to add ions to the electrolyte as
referenced earlier in the work of Moji and Marceau.[5] These authors
say that current density control is one of the keys to the process
of creating a porous film. It is quite simple and requires only
the addition of enough ionizable fluoride ions to the solution to
maintain a consistent current density and oxide dissolution rate.
Unfortunately, as was indicated earlier, fluoride is the wrong ion
to choose since it creates a weak boundary layer at the interface
of the oxide and the metal or alloy. Details on the creation of
strippable oxide film on several valve metals is reported separately.[8]
In the present work, several soluble compounds were added to the

TABLE II

BREAKDOWN (SPARKING) VOLTAGE
FOR METALS AND ALLOYS IN H_3PO_4

H_3PO_4 Concent.	1M	0.1M	0.05M	0.025M
Ti6Al4V	90V	180V	220V	320V
Al	90V	160V	190V	230V
6061 Al	90V	160V	210V	320V
Ta	130V	220V	280V	430V

conventional anodizing solutions to create porous films. One electrolyte that produced porous films was 0.2 gram per liter of lithium nitrate in an electrolyte made up of two grams of phthalic acid per liter. A comparison of the wetting characteristics of oxides formed under identical conditions with and without the lithium nitrate are shown in Figure 8. In Figure 8A, the Ti6Al4V alloy was anodized for two minutes at 64 volts in phthalic acid. Figure 8B shows spectra from an anodized specimen of the same alloy anodized two minutes at 64 volts in phthalic acid with 0.2 gram of lithium nitrate added. Each sample is marked with a nylon fine tip black marker above and below the original fluid meniscus, as shown by the dashed line on both samples. Here lithium nitrate was chosen for two purposes. First it provided ions that raised the current density and in addition it provided a marker ion for SIMS analysis, which was in a portion of the spectrum in which ions were not normally observed. Also, the alkali metals are by far the most sensitive of all of the elements that can be observed by secondary ion mass spectrometry. Figure 9 shows a positive SIMS spectrum from a typical porous film obtained from the phthalic acid and lithium nitrate. The area of the spectrum is noted where lithium would occur, atomic masses 6 and 7. These results and others with different additives indicate that the lithium nitrate and other additives change the anodized film, but do not enter into the formation of the film itself. Perhaps still other selected additives could be included in a bath which would enter the oxide to provide desirable features, such as phase stabilizers in anatase which has many vacancies.

Creation of porosity in anodized films can in some cases improve adhesion as reported earlier.[5] Figure 10 shows crack exten‑ on data for Ti64 which had been anodized to form both dense and porous oxides. The porous oxide produced better initial bond strength and showed a smaller amount of cracked growth during testing.

SECTION IV
SUMMARY

Porous films on titanium alloys have been shown to produce superior adhesion characteristics compared to dense oxides.[5] Porosity also improves wetting and spreading characteristics. Oxide porosity may be achieved with an increasing current density in the anodization bath by increasing the voltage, increasing the temperature, increasing the concentration of the electrolyte, or by the addition of other current carrying ions to the electrolyte. Fluorine should be scrupulously avoided in such solutions because of the tendency to form very weak boundary layers.

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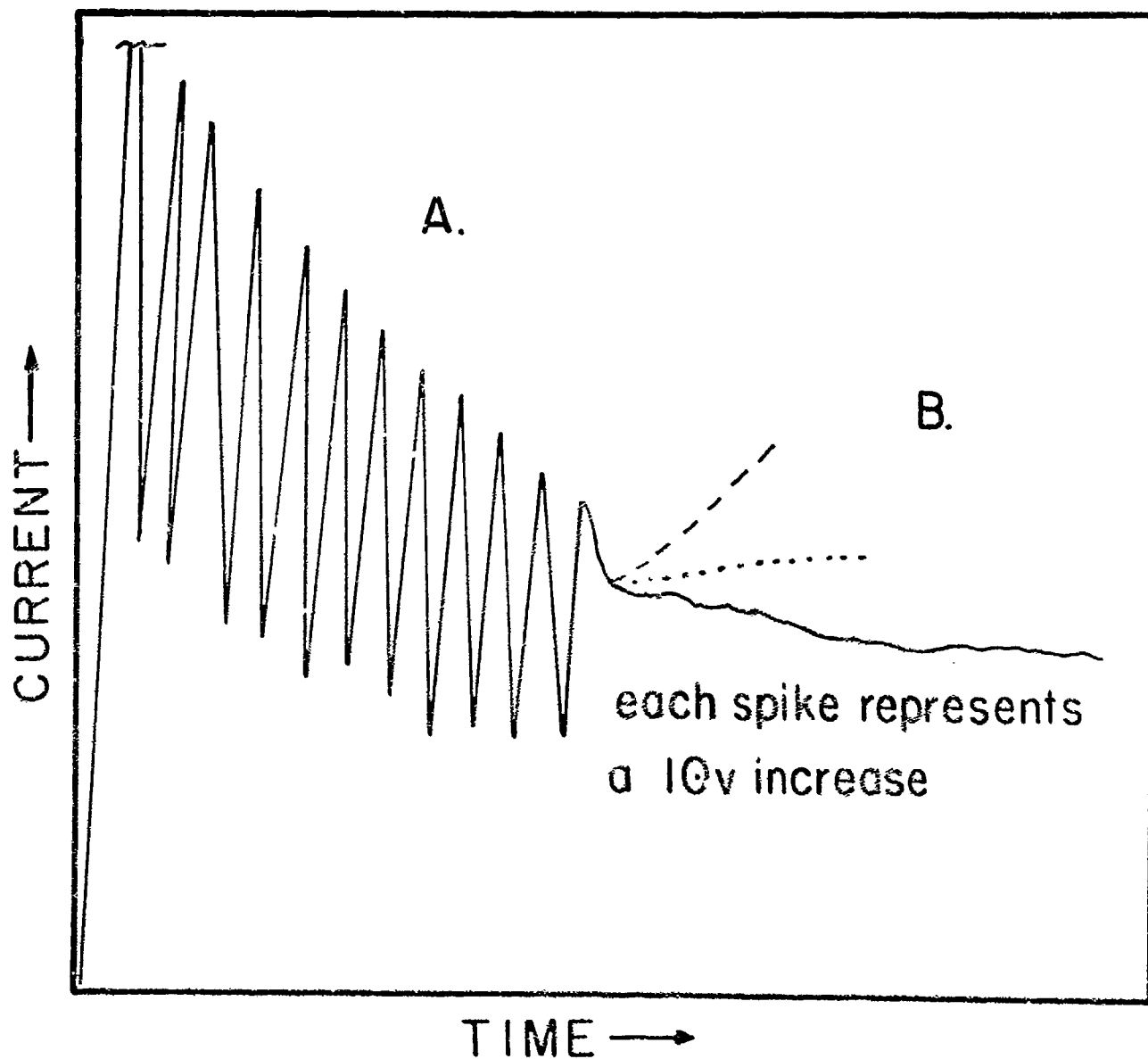
Figure 1. Typical time versus current curve for anodization of Ti 6Al 4V. When voltage increased in ten-volt steps (A region) until region reached where current no longer follows a sharp rise and decay form (Region B).
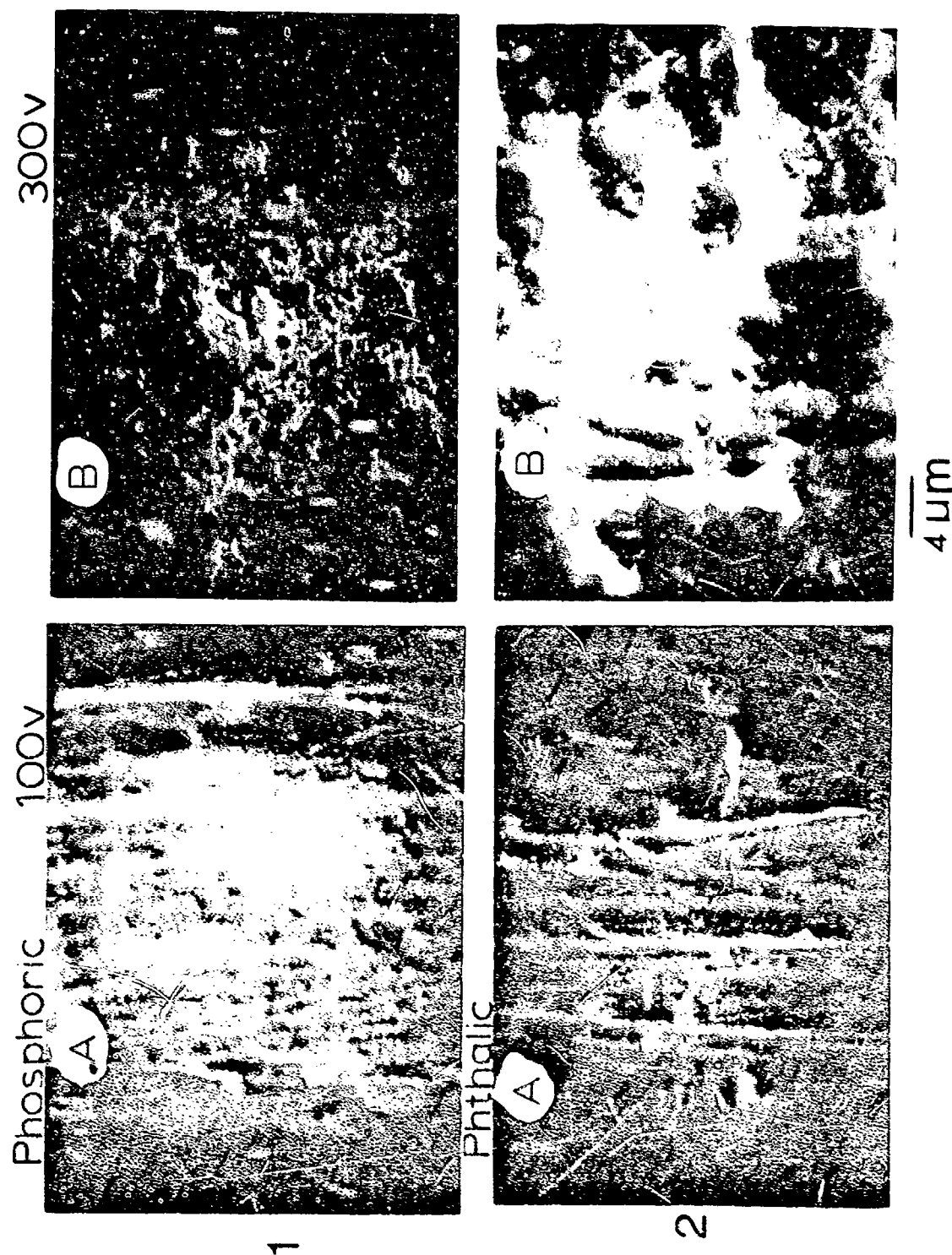
Figure 2. Scanning electron micrographs of Ti 6Al 4V anodized in 1.0 molar phosphoric acid and in two gram per liter phthalic acid. Sample A was anodized at 100 volts and Sample B at 300 volts.
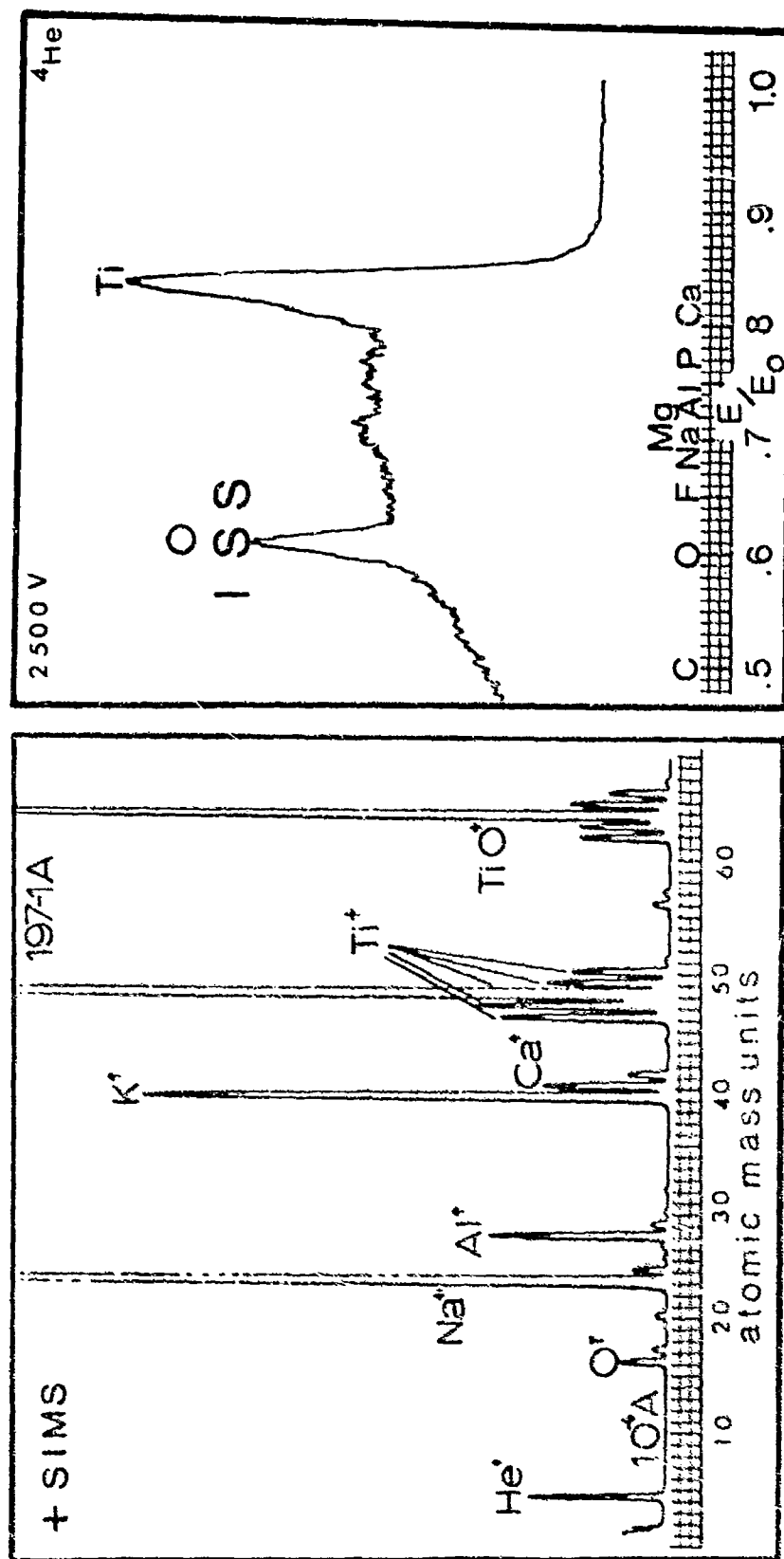
Figure 3. ISS and +SIMS data for Ti 6Al 4V anodize at 50 volts in mixture of Na_2HPO_4 and H_3PO_4 to form pH 7 solution.
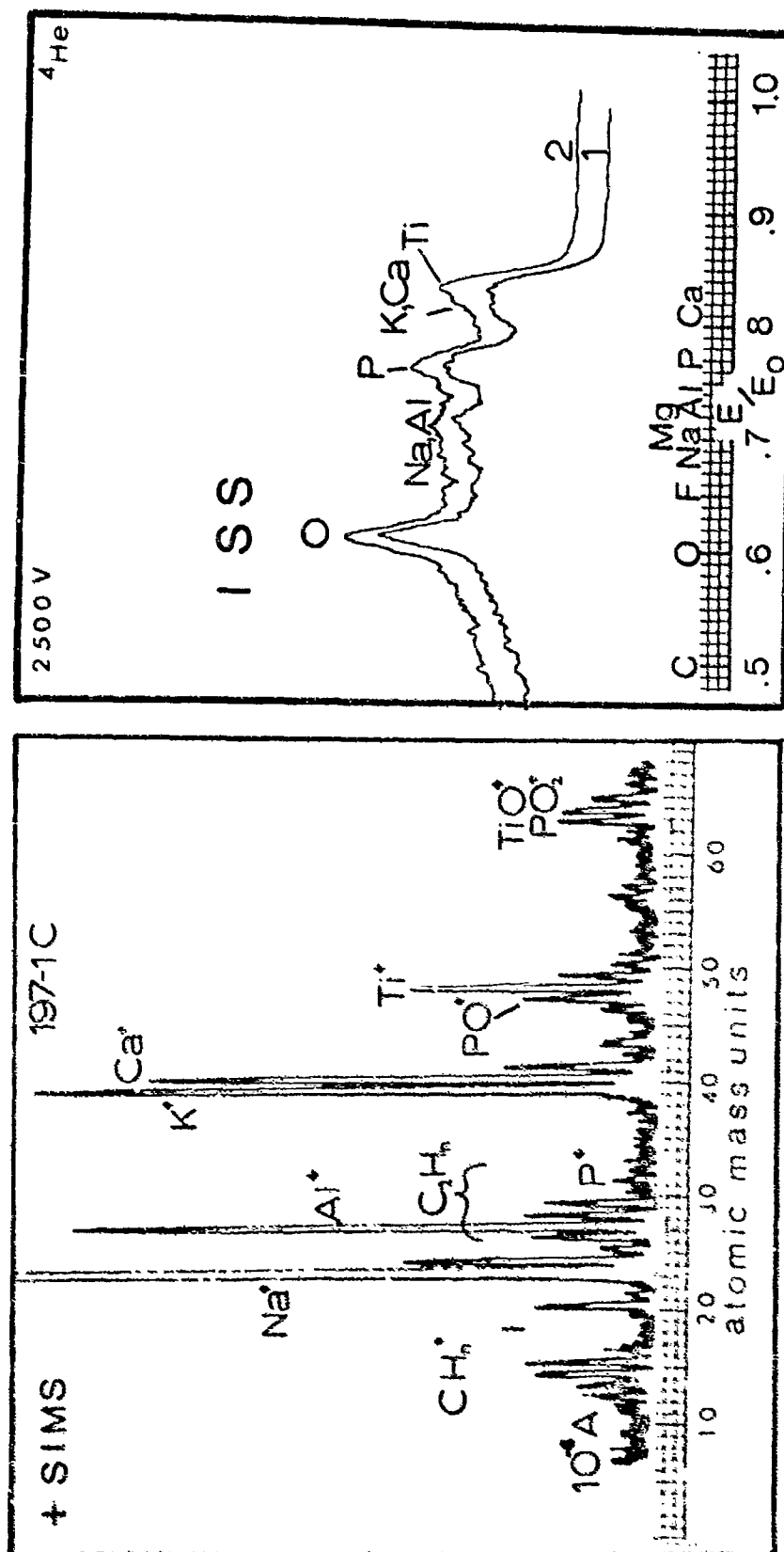
Figure 4. Same as Figure 3, but anodized at 100 volts.
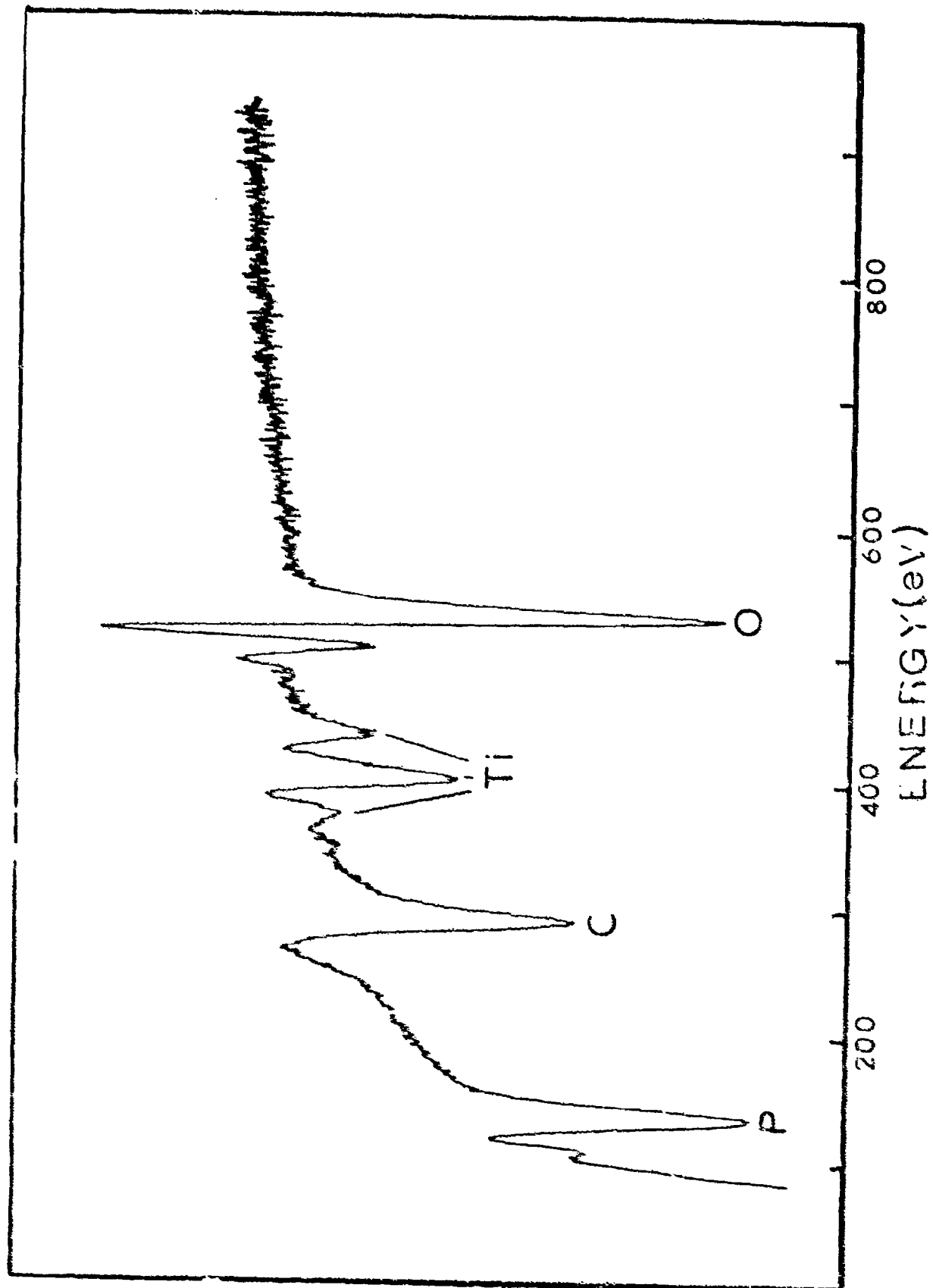
Figure 5. AES from porous film formed at 100 volts in pH 7 mixture of Na_2HPO_4 and H_3PO_4.
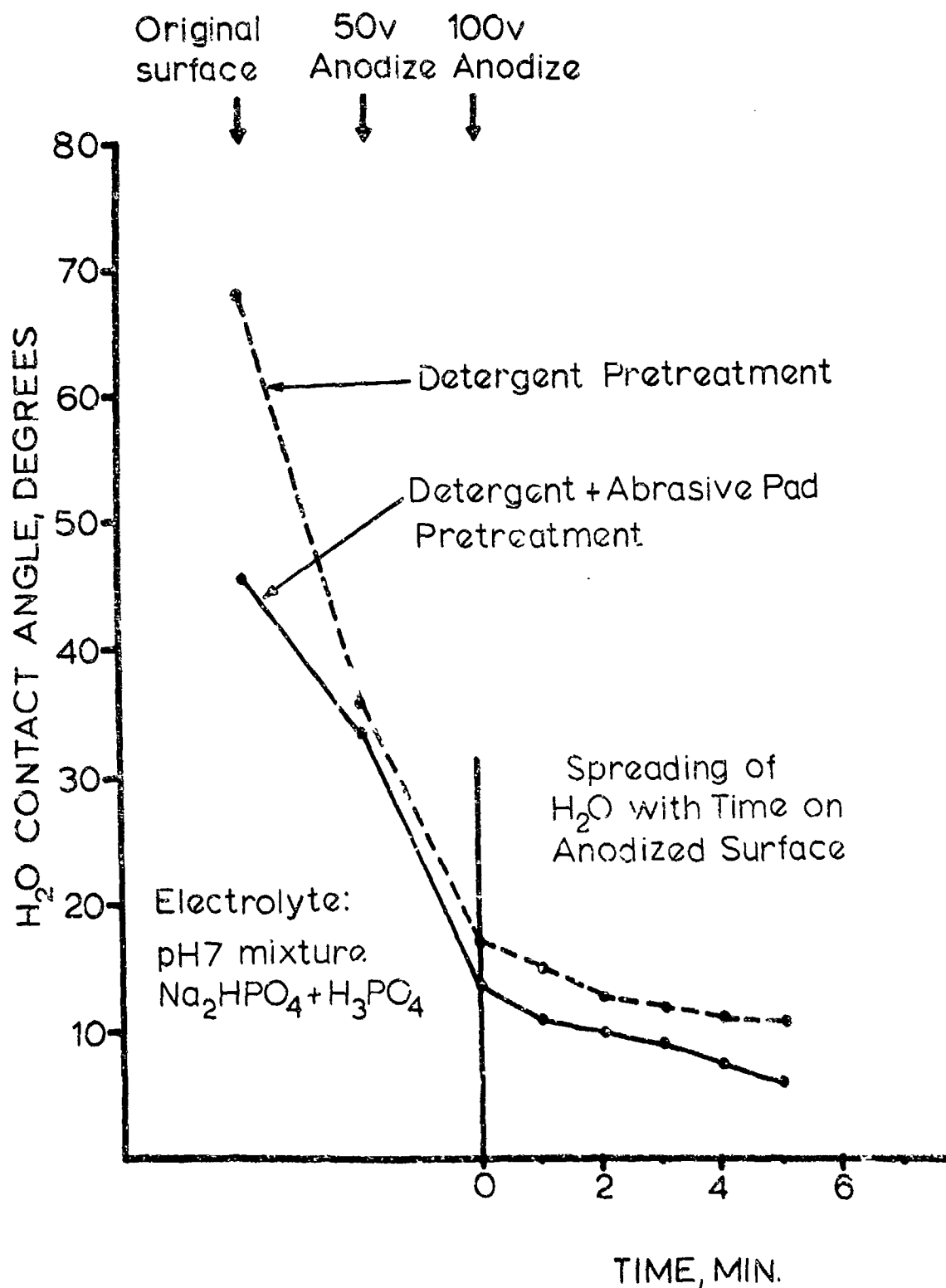
Figure 6. H_2O contact angle for two specimens of Ti 6Al 4V anodized at 50 volts and 100 volts in pH 7 mixture of Na_2HPO_4 and H_3PO_4. Spreading of the H_2O with time is also shown.
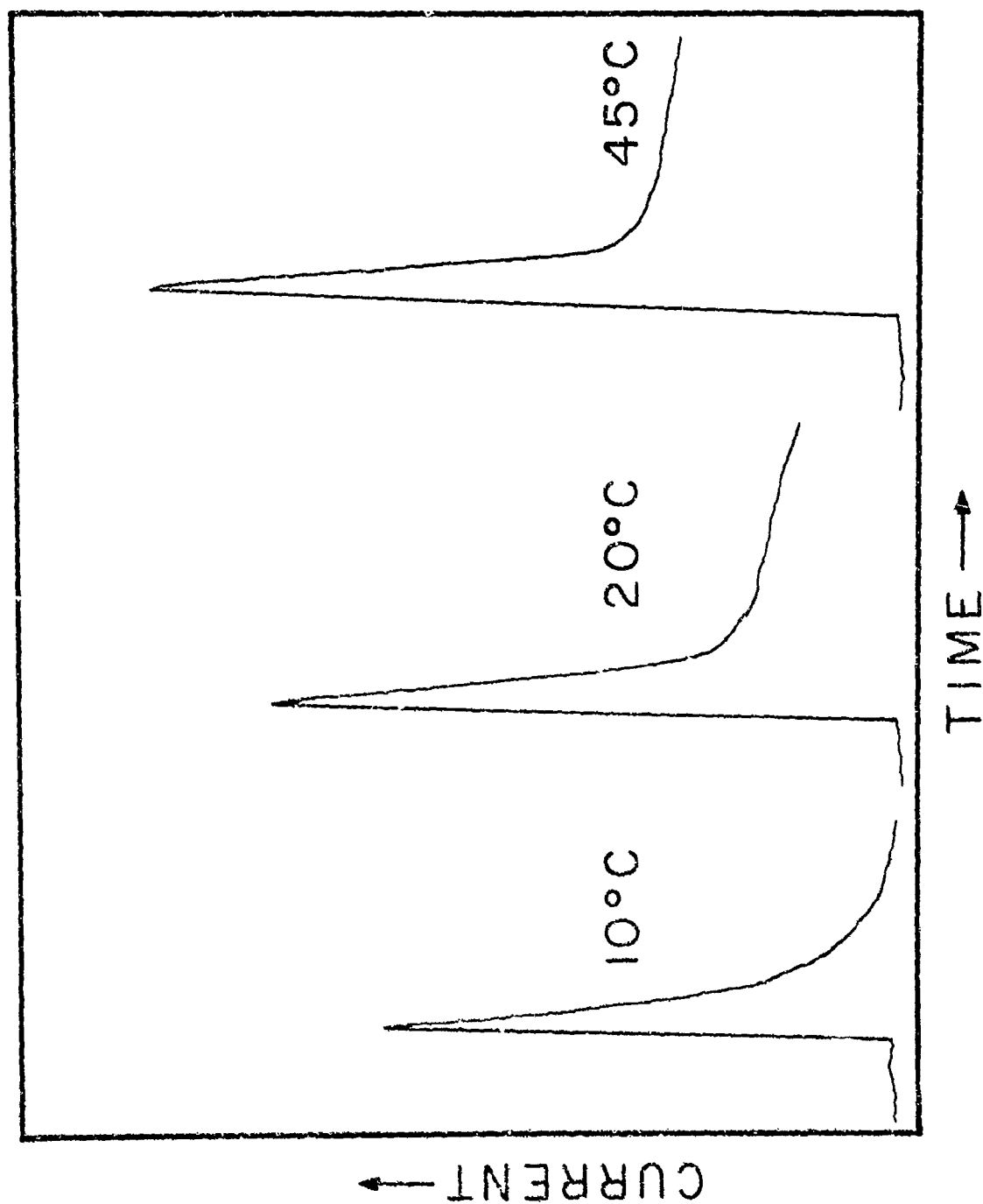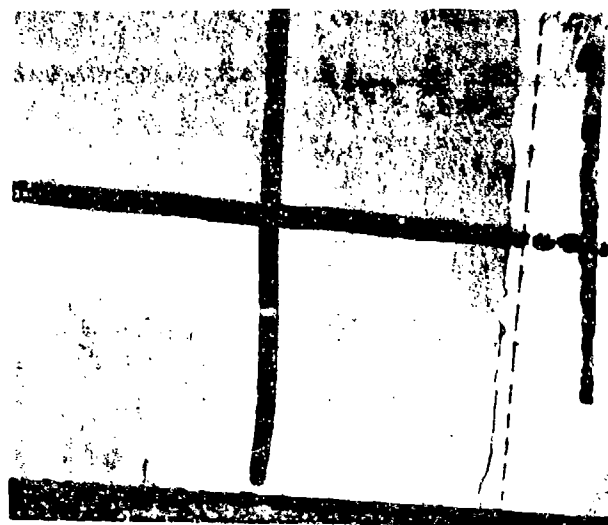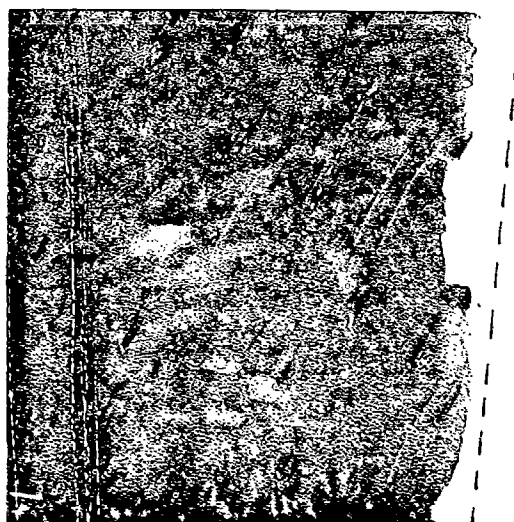
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Figure 7. Effect of temperature on time versus current curve for anodization Ti 6Al 4V in 0.5 molar H_3PO_4.

A

4 m m

B

Figure 8. A. Ti 6Al 4V alloy anodized at 64 volts for two
minutes at two grams per liter phthalic acid. B.
Ti 6Al 4V alloy anodized at 64 volts for two
minutes at two grams per liter phthalic acid with
0.2 gram per liter lithium nitrate added. Fine
nylon tip black marker on each above and below
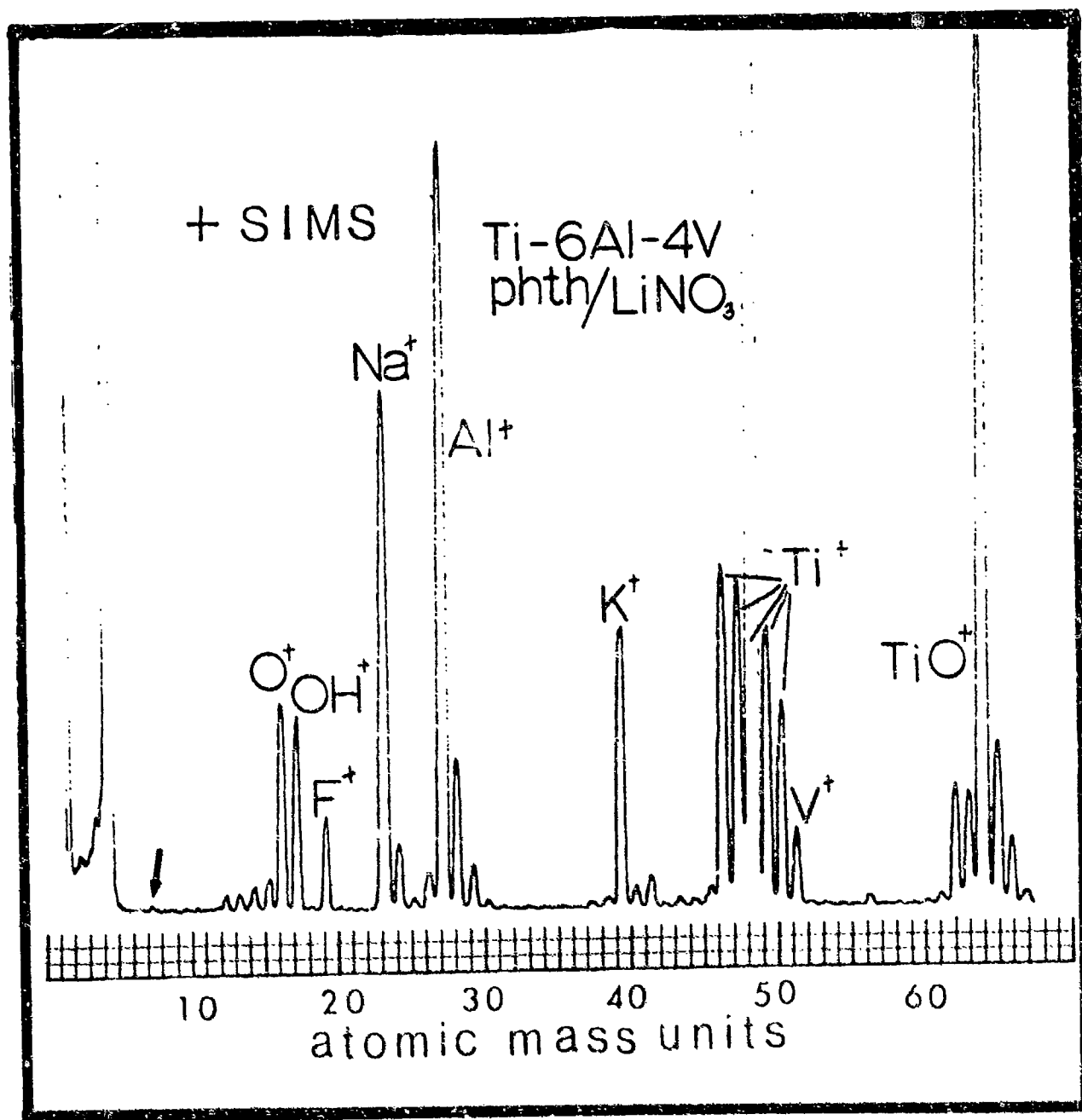area where the specimen entered the anodized
electrolyte.

Figure 9. Positive secondary ion mass spectrum of anodized film on Ti 6Al 4V formed in two gram per liter phthalic acid and 0.2 gram per liter lithium nitrate.
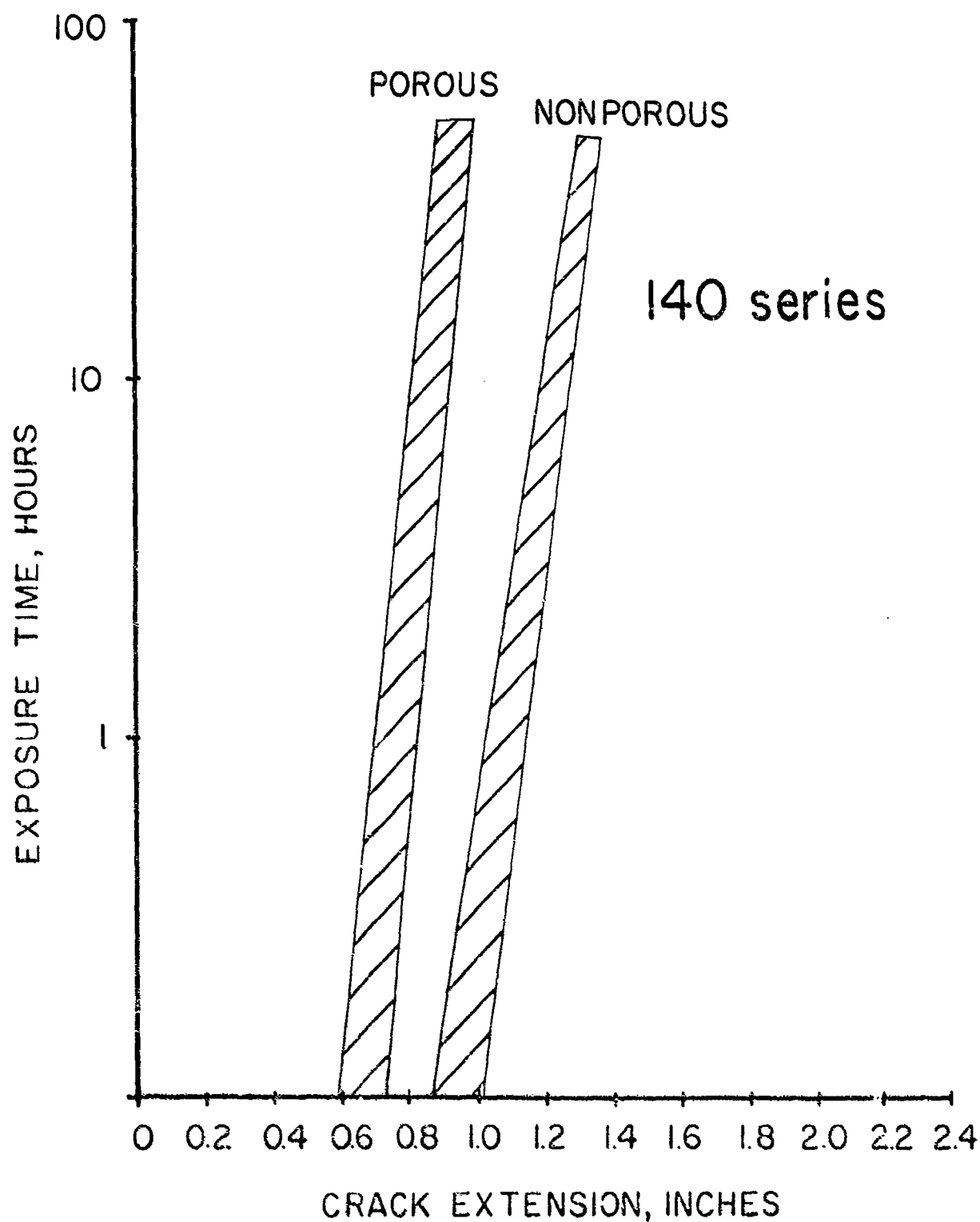
Figure 10. Crack extension data for samples held at 160°F and 95% R. H. Samples treated similarly but porous oxides achieved in electrolyte to which LiNO$_3$ was added.

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